Supporting Information

Crystal structure, spectroscopic, DNA binding studies and DFT calculations of a Zn(II) complex containing pyridoxal appended Schiff base and its application in Bioimaging of Zn(II)

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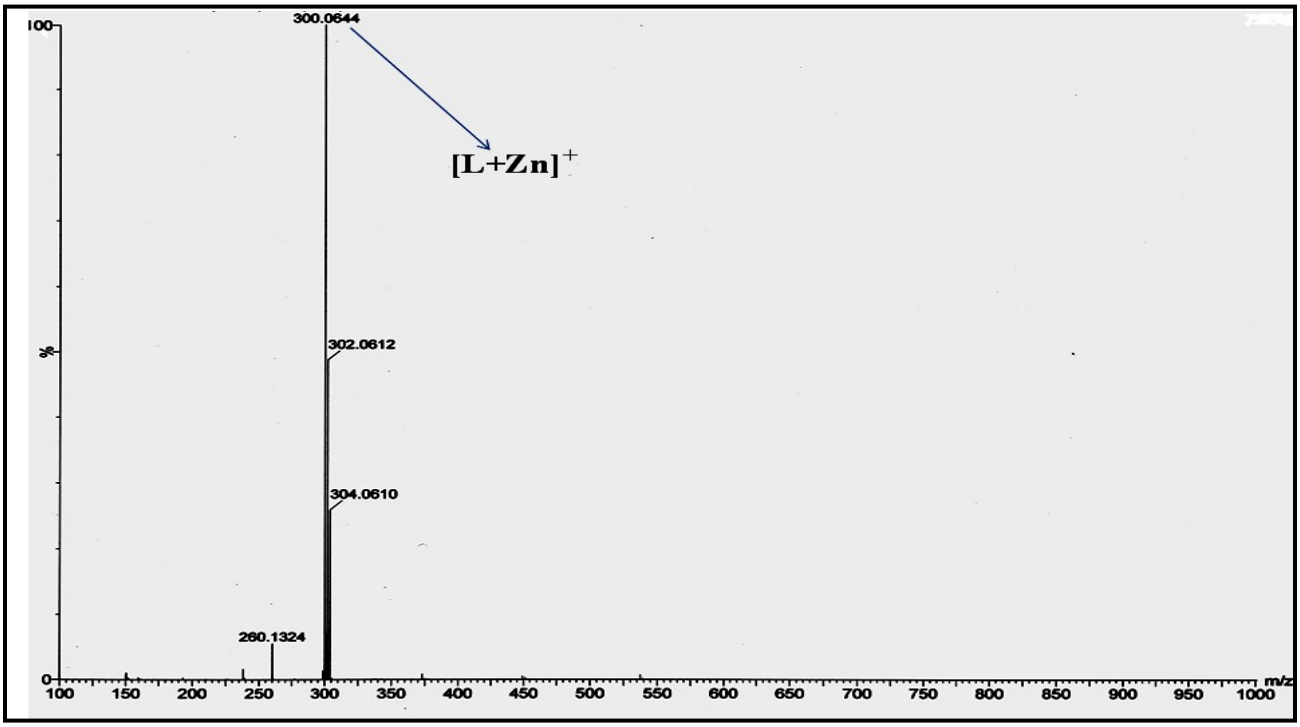

Figure S1: Mass spectrum of Complex **1**.

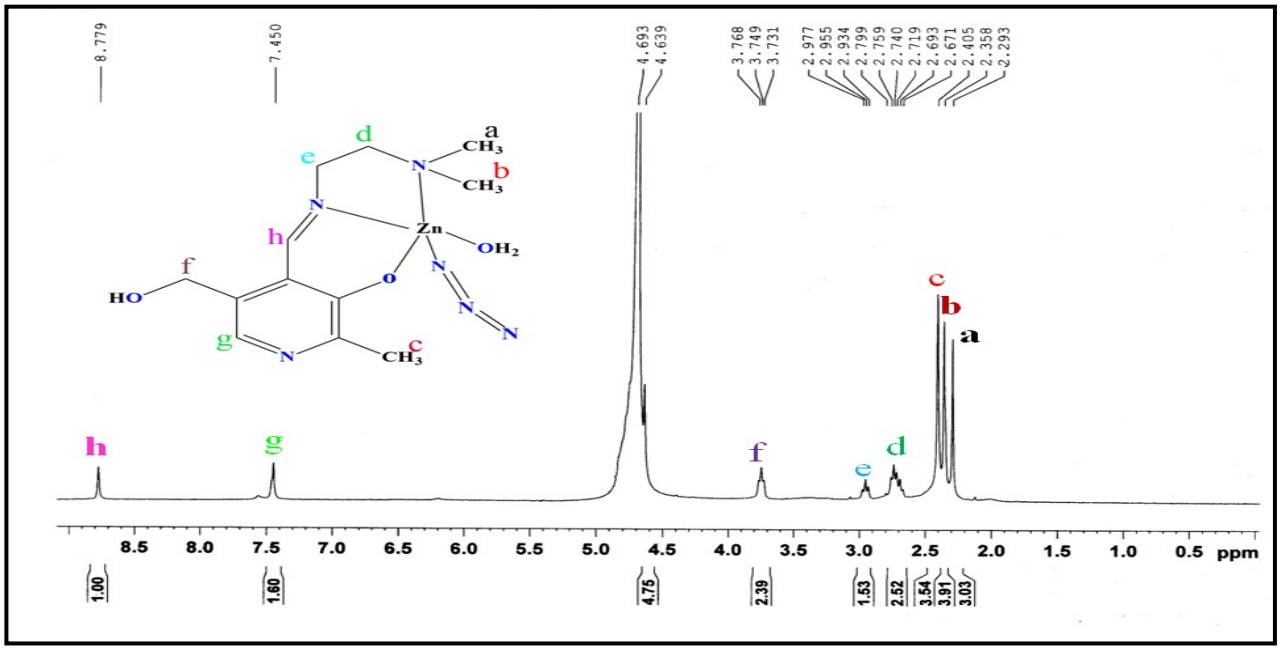

Figure S2:^{1}H NMR spectrum of Complex **1**.

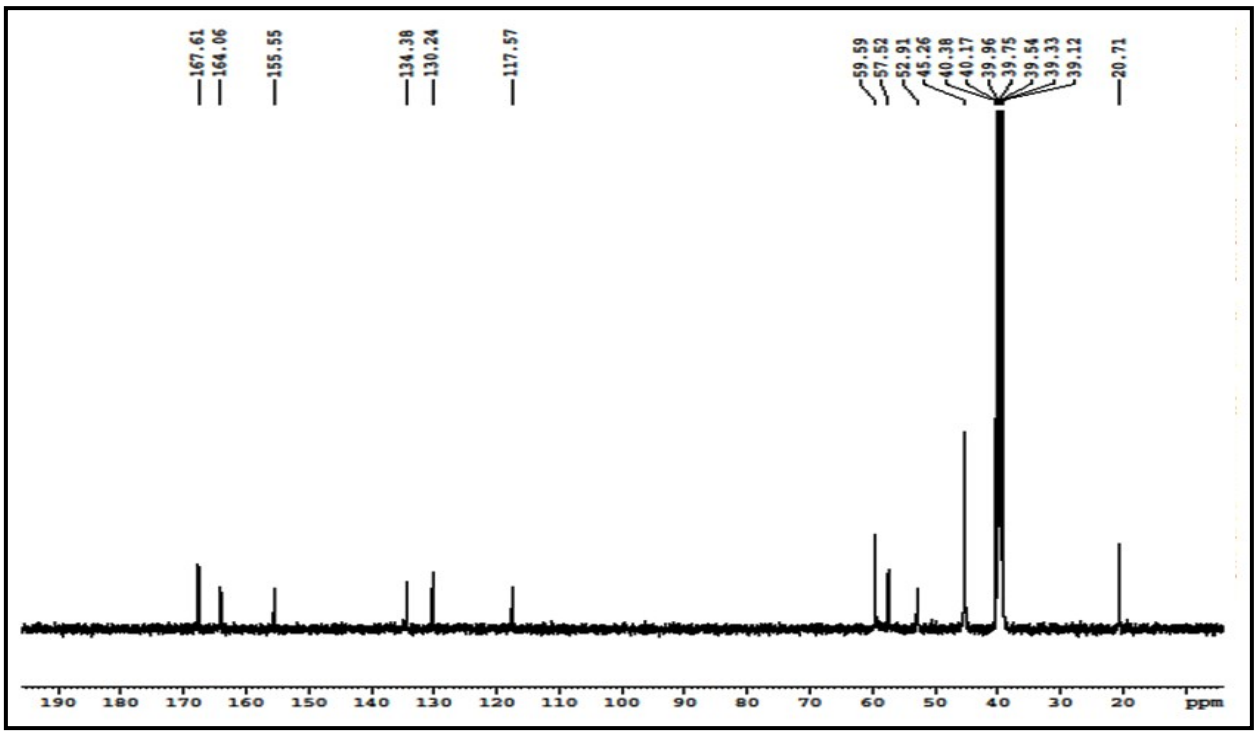

Figure S3: ^{13}C NMR spectrum of Complex **1**.

Table S2: Analysis of Hydrogen Bonds

Serial No.	D-H---A	D-H (Å)	H---A (Å)	D---A (Å)	D-H---A (°)
1	O2-H2A---N3[a]	0.82	2.01	2.787(7)	157
2	O2-H2B---N6[b]	0.82(5)	1.90(5)	2.719(5)	176(6)
3	O3-H3---O1[c]	0.82	2.08	2.883(4)	168
4	C3-H3---O1	0.96	2.34	2.797(5)	109
5	C8-H8---O3	0.93	2.54	3.151(5)	124

Symmetry operations: a= 1/2+x,1/2-y,-1/2+z; b= 3/2-x,1/2+y,3/2-z; c= 1-x,-y,1-z

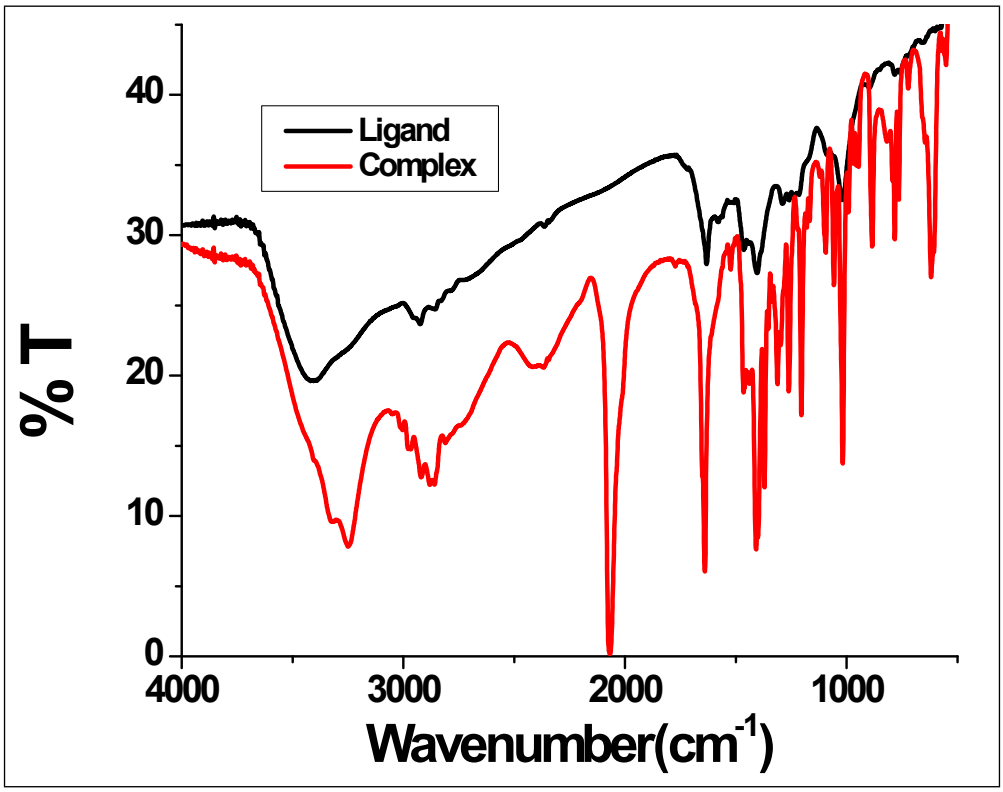

Figure S4: IR Spectra of ligand and the complex **1**.

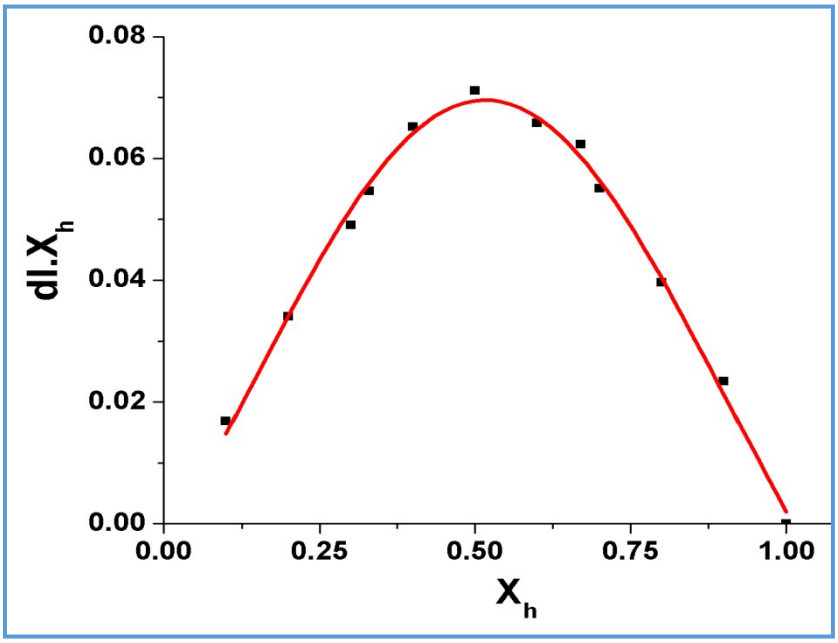

Figure S5: Job's plot of complex formation between ligand (host) and the Zn(II). X_h is the ligand mole fraction.

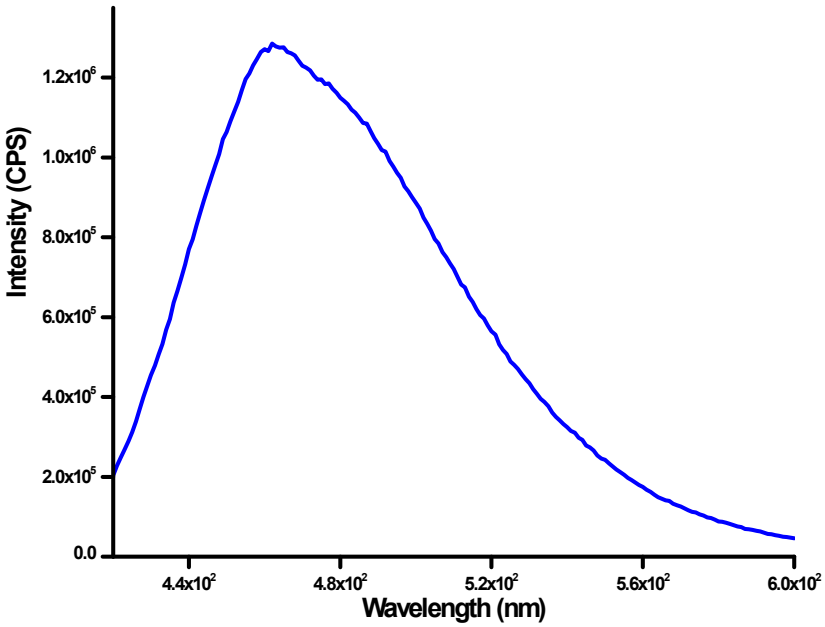

Figure S6: Emission spectra of complex **1** in 9: 1 methanol :water buffer (pH7.4, λ_{ex} 390 nm).

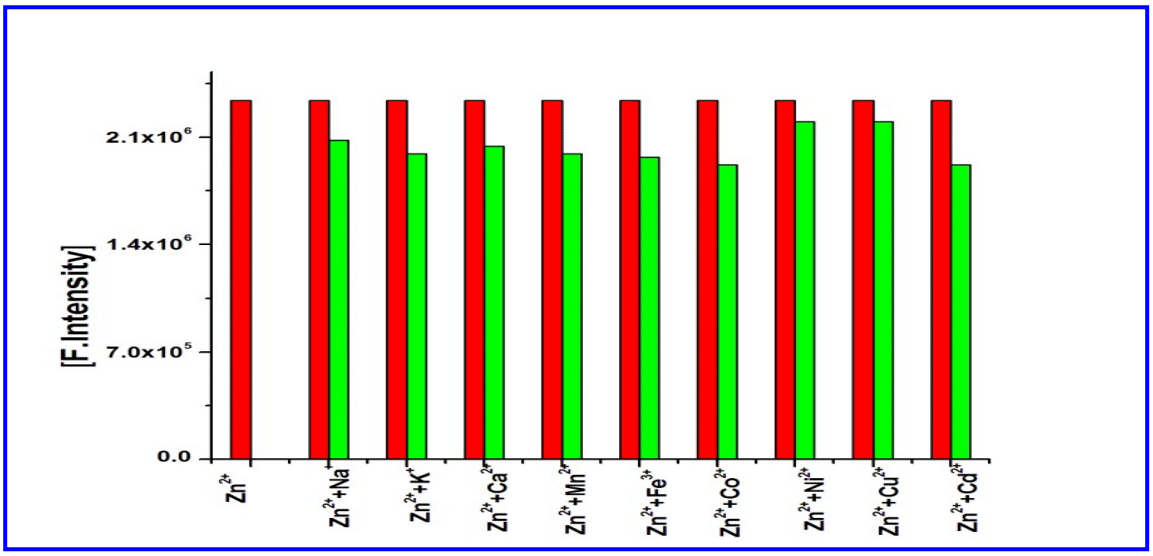

Figure S7: Red bars: Fluorescence Changes of HL (1×10^{-5} M) in the presence of 1 equiv of Zn(II) solution. Green bars: Enhanced emission upon the addition of different cations (3 equiv). All samples are prepared in 10 mMTris-HCl buffer at pH 7.4 and excited at 385 nm.

Calculation of Binding constant and detection limit for Ligand with Zn(II)complex:

The binding constant value of Zn(II) with ligand has been determined from the emission intensity data following the modified Benesi–Hildebrand equation, $1/\Delta I = 1/\Delta I_{max} + (1/K[C])(1/\Delta I_{max})$. Here $\Delta I = I - I_{min}$ and $\Delta I_{max} = I_{max} - I_{min}$, where I_{min}, I, and I_{max} are the emission intensities of ligand considered in the absence of Zn(II), at an intermediate Zn(II) concentration, and at a concentration of complete saturation where K is the binding constant and [C] is the Zn(II) concentration respectively. From the plot of $[1 / (I_{min} - I)]$ against $[C]^{-1}$for ligand, the value of K has been determined from the slope. As the plot of $1/ (I - I_{min})$ vs 1/[C]gives a straight line, indicates the 1:1 complexation of the sensor with Zn(II). The association constant (K_a) as determined by fluorescence titration method for the ligand with Zn(II) is found to be 1.8×10^5 M^{-1}.

Calculation of the detection limit:

The detection limit DL of Ligand for Zn(II)was determined from the following equation:

DL = K* Sb1/S Where K = 2 or 3 (we take 2 in this case); Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

For Ligand with Zn(II):

From the Intensity vs. Zn(II) graph, we get slope = 4.25327E11, and Sb1 value is 62770.41679.

Thus using the formula, we get the Detection Limit = 2.95×10^{-7} M

Y = A + B * X			
Adj.R Square	0.99359		
		Value	Standard error
A	Intercept	4.21325E-7	1.59181E-8
B	Slope	2.33302E-12	1.6197E-13

a

Y = A + B * X			
Adj.R Square	0.99169		
		Value	Standard error
A	Intercept	-138936.96259	53683.53521
B	Slope	4.25327E11	2.46785E10

b

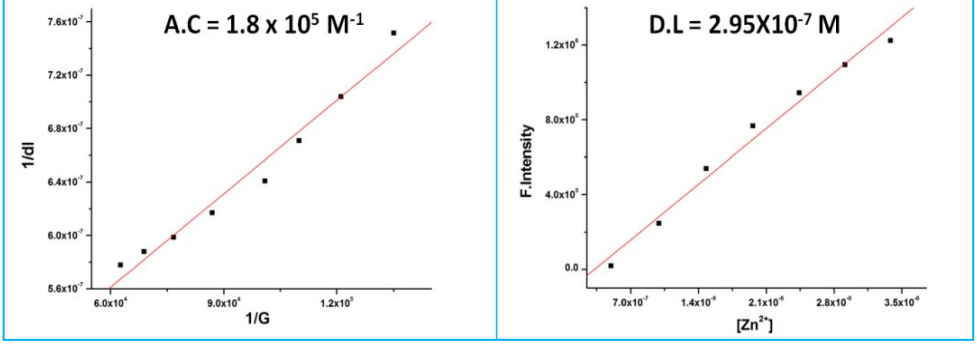

Figure S8: Association constant and Detection limit calculation Ligand with Zn^{2+}.

Figure S9: Fluorescence Microscopic photographs of (a) *Candida albicans* cells treated with ligand, (b) *Candida albicans* cells treated with Zn(II) + followed by the ligand.

Table S2: DFT results of Complex **1.**

Complex **1** (optimized in Gas phase)

orbitals	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3
Energy(eV)	-6.27	-6.02	-5.81	-5.67	-1.96	0.01	0.41	0.64
Zn contributions	0.84	3.42	2.03	1.05	0.44	0.52	60.67	38.63

Atom name and number		Bond distance (Å)	Mayer bond order
1Zn	6N	2.105	0.33
1Zn	10O	2.02	0.378
1Zn	12O	2.233	0.28
1Zn	15N	2.014	0.497
1Zn	26N	2.308	0.23

Complex**1** (optimized in MeOH):

orbitals	HOMO -3	HOMO -2	HOMO -1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3
Energy(eV)	-6.26	-5.96	-5.9	-5.6	-1.76	0.18	0.29	0.7
Zn contributions	1.54	2.26	1.89	0.91	0.35	2.51	55.32	45.31

Atom name and number		Bond distance (Å)	Mayer bond order
1Zn	6N	2.136	0.326
1Zn	10O	2.032	0.402
1Zn	12O	2.155	0.294
1Zn	15N	2.053	0.424
1Zn	26N	2.289	0.216

Table S3: TD-DFT calculations of Ligand and Complex**1**.

	Experimental wave length (nm)	Wave length obtained from TD-DFT (nm)	Oscillator strength (f)	Contributing orbital(s)	Percentage contribution
Zn(II) Complex (opt in Gas)	385	395.166	0.0073	HOMO->LUMO	88%
		376.5172	0.0041	H-3->LUMO	78%
		368.4059	0.0337	H-2->LUMO H-1->LUMO	24% 57%
		349.4556	0.0798	H-2->LUMO	72%
	270	277.0949	0.0061	H-5->LUMO	63%
		262.8994	0.0955	H-4->LUMO	57%
Zn(II) Complex (opt in Methanol)	385	374.7418	0.0041	H-3->LUMO H-2->LUMO	39% 52%
		362.4926	0.1614	HOMO->LUMO	80%
		343.235	0.0186	H-1->LUMO	94%
	270	282.7894	0.0077	H-4->LUMO	70%
		264.8255	0.1046	H-5->LUMO	56%

Optimized Geometries

Complex in gas:

Zn	4.42419100	3.36639100	6.39485700
C	4.48753000	3.35745700	3.42044500
H	3.40876400	3.17836600	3.32268000
H	4.95690900	3.08734600	2.46395900
C	6.52257600	0.84470000	5.34617500
N	5.00286700	2.57390300	4.53261200
C	6.54501500	1.24457000	6.72039500
O	6.05588100	-1.05062300	2.94943500
H	5.57547600	-1.64983500	3.54315900
O	5.91667700	2.27401700	7.20691000
N	8.02209600	-0.61780100	7.23738500
O	4.81057100	4.43667600	8.31636700
H	5.42511600	3.72971500	8.59806800
C	7.27914600	-0.30623900	4.96198000
N	2.59929200	3.09996200	7.20511400
C	4.76271300	4.83887700	3.72831500
H	5.84766700	4.98338500	3.75483600
H	4.35718200	5.48325100	2.93315800
C	7.34795600	0.45063800	7.62247300
C	7.33651400	-0.80835100	3.53479500
H	7.81022000	-0.07246500	2.87367000
H	7.96218900	-1.71216100	3.50205100
C	5.83187000	1.60105200	4.32410700

H	6.03843800	1.31970400	3.28872900
N	1.53917800	2.86908000	6.66362600
N	4.22384700	5.23501100	5.05475100
C	7.98005600	-0.98749500	5.93756300
H	8.55007700	-1.87907500	5.68123600
C	7.40710000	0.84570100	9.07353100
H	8.05147600	0.14781400	9.61229800
H	6.40788200	0.83795600	9.52684400
H	7.79933100	1.86383700	9.19185300
N	0.50992900	2.66253500	6.18059200
C	2.78296200	5.55949300	4.96820700
H	2.40012300	5.77002300	5.96880200
H	2.21997800	4.71211700	4.57003400
H	2.61465800	6.43496200	4.32178100
C	4.96054100	6.39296000	5.59868400
H	6.02038000	6.14203000	5.69672300
H	4.57389900	6.63184700	6.59176500
H	4.86142900	7.27728800	4.94980600
H	3.93189700	4.17218000	8.65563300

Complex in MeOH:

Zn	4.65531500	3.60062800	6.38216000
C	4.86386200	3.55267500	3.32776600
H	3.91261700	3.16150400	2.94186000
H	5.60219800	3.46284500	2.51925900

C	6.41868600	0.80361200	5.36754000
N	5.24919000	2.77289000	4.50501100
C	5.94166700	0.88456800	6.71512300
O	7.00085500	-0.58236200	2.59235900
H	6.42429000	-1.34253800	2.83650900
O	5.12652600	1.78571500	7.16457000
N	7.24138200	-1.09740400	7.28789900
O	6.36596800	4.78234200	6.94974000
H	7.25518800	4.38813100	6.80051100
C	7.32873400	-0.24504700	5.02687900
N	3.21751200	4.13589700	7.74694400
C	4.71517100	5.02470500	3.72148300
H	5.70345100	5.43083800	3.96455100
H	4.31205000	5.60284600	2.87460600
C	6.40408000	-0.13387700	7.63593000
C	7.94496400	-0.39710200	3.64917400
H	8.50768000	0.50362300	3.37529200
H	8.66186900	-1.23067500	3.67856100
C	5.98742500	1.72155900	4.33370300
H	6.29901900	1.46733900	3.31726000
N	2.97415100	3.64064900	8.81505400
N	3.86654900	5.18049300	4.92576200
C	7.69305200	-1.14514800	6.01006000
H	8.38841300	-1.95346900	5.78094000
C	5.91741100	-0.08254600	9.05925400

H	6.33144500	-0.92335800	9.62177900
H	4.82228200	-0.11676500	9.10576500
H	6.21296100	0.85656000	9.54359900
N	2.69184800	3.20570800	9.85632100
C	2.44523700	4.90169700	4.63587100
H	1.87694800	4.98425200	5.56475600
H	2.32491500	3.88570100	4.25010900
H	2.04304100	5.60956300	3.89441800
C	3.99370800	6.54334900	5.47685600
H	5.04007200	6.74076700	5.72104800
H	3.39942700	6.60995200	6.39166600
H	3.63935600	7.30066100	4.76020700
H	6.36108700	5.05002200	7.89724100